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(54) Title: FLOCCULATING AGENT CONTAINING ALUMINIUM AND A POLYBASIC CARBOXYLIC ACID (57) Abstract <p>A method for clarifying bodies of water and eliminating algal bloom caused by planktonic algae in water harboring biological systems is described using a novel flocculating agent prepared in an aqueous solution containing a combination of a monomeric or polymeric aluminum salt and a polybasic carboxylic acid; the method results in complete clarification of a body of water without harming fish that may be present; a preferred flocculating agent described includes a combination of polymeric aluminum hydroxy-chloride and L-(+)-tartaric acid.</p>		

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FLOCCULATING AGENT CONTAINING ALUMINUM
AND A POLYBASIC CARBOXYLIC ACID

Field of the Invention

5 The present invention relates to a method of clarifying bodies of water containing algal blooms caused by planktonic algae without harming fish that may be present by treating such waters with a flocculating agent.

Background of the Invention

10 When fish are kept in garden pools or ponds, and in ponds in open surroundings, mass-multiplication of planktonic algae gives rise to algal blooms. This phenomena represents a serious problem both aesthetically and biologically. In addition, the problem can also
15 occur albeit with a lesser intensity in outdoor ponds that do not harbor fish, and even in indoor holding systems, e.g. aquariums. Efforts have and are being made to combat these algal blooms.

20 Besides the use of herbicides, flocculating agents have been used in recent years for removing the photo-plankton quasi-mechanically. In particular, flocculating agents based on monomeric and polymeric aluminum salts have proved to be very effective.

25 Despite the useful effect that was achieved, i.e. the clarification of the water, the treatment of biological waters and fish-keeping systems with solutions of aluminum salts entails a number of disadvantages such as harmful side effects, their severity varying according to the aluminum salt chosen.

30 Thus, for example, large or repeated doses of aluminum salts will reduce the carbonate hardness, or

alkalinity, of the water being treated by taking-up available OH ions for the purpose of precipitating aluminum hydroxide.

5 Since dosing with aluminum salts entails the risk that the water will become insufficiently low in carbonate hardness or total alkalinity, the action taken to combat the algae will then become toxic for fish. This limits the single-application dose and the total number of doses that can be applied.

10 Many experiments have shown that, in fresh waters with a carbonate hardness of approximately 3°dH, or an alkalinity of approximately 1 mVal/l, or lower, there ceases to be any guarantee that the use of aluminum salts will be safe, and the occurrence of lethal toxic effects on fish becomes possible.

15 Even reducing the dosage of Al^{3+} ions, e.g. from 8 mg/l to 2 - 3 mg/l, fails to bring about any significant reduction in the toxicity, given that the above-mentioned chemical conditions of hardness and alkalinity prevail in the water. Although not wishing to be bound by theory, the reason for this resides in the mechanism of the toxic effect.

20 At the typical pH values that generally prevail, for example between about 6.5 and 8.5, the Al^{3+} ion species present in solution no longer have toxic effects. However, so-called primary $Al(OH)_3$ flocs form at the beginning of the reaction in which the very sparingly soluble aluminum hydroxide is produced, and these primary flocs remain in colloidal solution.

30 These primary flocs, which are still positively charged, find their way onto the negatively charged gill tissues of the fish, and irritate the gills. The fish can suffocate as a result of an increase in the production of mucus by their gills.

35 These harmful effects become all the more powerful the longer the primary-floc formation phase lasts. Up to

now, there was no way of selectively minimizing this vicious side effect of the $\text{Al}(\text{OH})_3$ flocculation, as employed for eliminating algal blooms. Reliable protection was offered only by higher carbonate hardness, above 3°dH, or alkalinities above 1 mVal/l. However, most garden ponds exhibit lower values, especially in years of high rainfall, and thus turn a flocculation treatment with aluminum salts into a considerable and incalculable risk as far as the fish are concerned.

Some aluminum-free flocculating agents, e.g. with organic polymers, would certainly be usable under soft-water conditions, but would give rather unsatisfactory results as regards clarification.

There thus remains a need for an efficient flocculating agent to remove algal blooms in garden pools or ponds and other interior systems harboring fish without the serious toxicity effects on fish.

SUMMARY OF THE INVENTION

The present invention relates to the object of minimizing the harmful effects associated with the flocculation treatment of algal blooms by means of polymeric aluminum hydroxy-chlorides, e.g. with the empirical formula $\text{Al}_2(\text{OH})_5\text{Cl}$. The present invention concerns the surprising finding that addition of organic carboxylic acids that have two or more protons brings about significant improvements and beneficial effects when combined with an aluminum salt.

Accordingly, the present invention is a new flocculating agent containing an aqueous solution of a monomeric or polymeric aluminum salt and a polybasic organic carboxylic acid in a molar ratio of aluminum ion to carboxylic acid of about 0.5:1 to about 50:1.

A second aspect of the present invention is a method of eliminating algal bloom in waters harboring biological systems comprising treating said waters with an effective

amount of a flocculating agent comprising an aqueous solution of a monomeric or polymeric aluminum salt and a polybasic organic carboxylic acid in a molar ratio of aluminum ion to carboxylic acid of about 0.5:1 to about 50:1.

Another aspect of the present invention is a method of flocculating planktonic algae in fresh waters down to a carbonate hardness of about 1°dH and an alkalinity of about 0.36 mVal/l without harming fish which comprises treating said waters with an effective amount of a flocculating agent as described above.

Still another aspect of the present invention is a method of clarifying a body of water contaminated with an algal bloom comprising treating said body of water with an effective amount of a flocculating agent as described above.

Detailed Description of the Preferred Embodiments

The invention describes novel flocculating agents for eliminating bloom phenomena in waters harboring biological systems, as caused by planktonic algae.

The agents contain an aluminum salt, which may be monomeric or polymeric, and a polybasic organic carboxylic acid, in molar ratios (Al:carboxylic acid) of 0.5:1 to 50:1, preferably 2:1 to 10:1

The compositions of the agents are adjusted with a view to obtain desired product range, and to ensure that each specific combination will be stable. The quantity of organic acid necessarily follows from the dosage requirement, and from the composition of the agent in question.

Applied in the dosages specified, the agents according to the invention enable the following novel effects to be achieved:

1. Flocculation of planktonic algae in fresh waters (algal bloom) is possible without harming fish, down to carbonate hardnesses of 1°dH and alkalinities of 0.36 mVal/1.
- 5 2. Flocculation is accompanied by a synergistic effect which
 - a) accelerates floc formation,
 - b) reduces the dosages of aluminum necessary for achieving comparably good clarification results
10 (especially when the pH is below 8.0),
 - c) and, by virtue of the smaller quantity of Al^{3+} ions, results in reduced depletion of the carbonate hardness, or alkalinity.

15 The flocculating agent of the present invention is a combination of monomeric or polymeric aluminum salts with a polybasic carboxylic acid.

A monomeric or polymeric aluminum salt includes a trivalent aluminum salt in monomeric or polymer form. The preferred salt is aluminum hydroxy-chloride in both
20 monomeric and polymeric form. Also of value are, for example, non-polymeric aluminum salts such as aluminum chloride or aluminum sulfate. These salts are all commercially available.

25 A polybasic carboxylic acid is an organic carboxylic acid having at least two active protons. Included among polybasic organic carboxylic acids, are those commercially available and, as examples which have proved suitable as flocculating agents with aluminum salts are:

30 citric acid;
glycolic acid;
tartaric acid;
maleic acid;
hydroxymaleic acids;
hydroxytartaric acids;

malonic acid;
malic acid;
lactic acid (α -hydroxypropionic acid);
tartronic acid;
5 sugar acids, such as gluconic acid;
saccharic acid;
glucuronic acid;
mucic acid; and
mannosaccharic acid.

10 Citric acid and, especially, tartaric acid bring about a very pronounced lowering of the toxicity limit that is associated with the carbonate hardness or alkalinity, i.e. from

$$CH = 3^{\circ}dH, \text{ or alkalinity} = 1.1 \text{ mVal/l}$$

15 to

$$CH = 1^{\circ}dH, \text{ or alkalinity} = 0.36 \text{ mVal/l}$$

An optimized solution of polymeric aluminum hydroxy-chloride, containing tartaric acid, can be used for flocculating algae even in water with a carbonate
20 hardness of $0.5^{\circ}dH$, or an alkalinity of 0.18 mVal/l , without harming garden-pond fish (koi, goldfish, golden carp and the like).

Of all the above-mentioned acids, L-(+)-tartaric acid, in combination with polymeric aluminum hydroxy-chloride has achieved the best results.
25

In contrast, concentrated solutions of polymeric aluminum hydroxy-chloride, on their own or in diluted form, react very sensitively to further additions, and such reactions are accompanied by precipitation effects
30 and extremely large increases in viscosity, even proceeding as far as solidification.

A solution containing only aluminum hydroxy-chloride, applied in a dosage giving the same aluminum concentration, caused toxic effects that were lethal even
35 at carbonate hardnesses of $2^{\circ}dH$, or alkalinities of 0.7 mVal/l .

The mixtures, according to the present invention, for example, of polymeric aluminum hydroxy-chloride and a polybasic organic carboxylic acid exhibit yet a further surprising effect.

5 In addition to the significant lowering of the carbonate hardness limit associates with the onset of toxicity, the use of the mixtures according to the invention is also accompanied by a flocculation synergism.

10 In cases involving algal blooms of equal intensity and pH values in the region of 7.5, the clarifying effect obtained with 50% of the Al^{3+} dosage in combination with a polybasic carboxylic acid already shows 60% of the effect obtained with the 100% dosage of the polymeric $Al_2(OH)_5Cl$
15 solution alone. Comparable results were also achieved with non-polymeric aluminum salts, e.g. $AlCl_3 \cdot 6H_2O$, $(SO_4)_3 \cdot 18H_2O$.

The agents according to the invention were unknown until now, as were the surprising effects that are
20 achievable through their use.

The dosage of the agents that have been described is generally selected with a view to ensuring that

0.5 to 50 mg/l Al^{3+} ,

preferably

25 2 to 10 mg/l Al^{3+}
are introduced into the water treated.

The following examples are illustrative of the present invention and are not to be construed as limiting thereon.

30 EXAMPLES

Agent Examples 1 - 3

500 ml of a concentrated solution of $Al_2(OH)_5Cl \cdot 2 \cdot 3H_2O$ (50% strength solution, 23.5% Al_2O_3) were mixed with

1. 50 g L-(+)-tartaric acid
- 35 2. 100 g L-(+)-tartaric acid

3. 150 g L-(+)-tartaric acid
and demineralized water, stirring all the while, and each
of these mixtures was thus diluted to 1 liter.

5 The resulting solutions were clear and slightly viscous;
they exhibited long-term stability and can be used for
flocculating planktonic algae.

Use Example

10 One of the agents itemized under Agent Examples was added
to garden pond water that had become discolored to the
extent of becoming green and non-transparent as a result
of an algal bloom, the dosage applied being 500 ml per
10,000 liters of pond water.

After 24 hours, the water was clarified to the highest
possible degree, and the flocculated-out algae settled.

15 The dosage specified above, and twice this dosage (1,000
ml per 10,000 l) can be applied without endangering pond
fish, down to carbonate hardnesses of 1°dH, or
alkalinities of 0.36 mVal/l.

WE CLAIM:

1. A flocculating agent comprising an aqueous solution of a monomeric or polymeric aluminum salt and a polybasic organic carboxylic acid in a molar ratio of aluminum ion to carboxylic acid of about 0.5:1 to about 50:1.
2. The agent of claim 1 comprising an aqueous solution of monomeric aluminum salt and a polybasic organic carboxylic acid.
3. The agent of claim 2 wherein the aluminum salt is aluminum hydroxy-chloride, aluminum chloride, aluminum sulfate or a mixture thereof.
4. The agent of claim 1 comprising a polymeric aluminum salt and a polybasic organic carboxylic acid.
5. The agent of claim 4 wherein the polymeric aluminum salt is an aluminum hydroxy-chloride.
6. The agent of claim 1 wherein the polybasic organic carboxylic acid is selected from the group consisting of citric, glycolic, tartaric, maleic, hydroxymaleic, hydroxytartaric, malonic, malic, lactic, tartronic, gluconic, saccharic, glucuronic, mucic, mannosaccharic and a mixture thereof.
7. The agent of claim 6 wherein the polybasic carboxylic acid is citric or tartaric acid.
8. The agent of claim 1 wherein the molar ratio of aluminum to carboxylic acid is about 2:1 to about 10:1.

9. The agent of claim 1 comprising an aqueous solution of polymeric aluminum hydroxy-chloride and L-(+)-tartaric acid.

5 10. The agent of claim 9 wherein the molar ratio of aluminum ion to tartaric acid is about 2:1 to about 10:1.

10 11. A method of eliminating algal bloom in waters harboring biological systems comprising treating said waters with an effective amount of a flocculating agent comprising an aqueous solution of a monomeric or polymeric aluminum salts and a polybasic organic carboxylic acid in a molar ration of aluminum ion to carboxylic acid of about 0.5:1 to about 50:1.

15 12. The method of claim 11 wherein the waters are treated with a flocculating agent comprising an aqueous solution having a concentration of about 0.5 to about 50 mg/l of aluminum ion.

13. The method of claim 11 wherein the flocculating agent is an aqueous solution comprising a monomeric aluminum salt and a polybasic carboxylic acid.

20 14. The method of claim 11 wherein the flocculating agent is an aqueous solution comprising a polymeric aluminum salt and a polybasic carboxylic acid.

25 15. The method of claim 11 wherein the polybasic carboxylic acid is selected from the group consisting of citric, glycolic, tartaric, maleic, hydroxymaleic, hydroxytartaric, malonic, malic, lactic, tartronic, gluconic, saccharic, glucuronic, mucic, mannosaccharic and a mixture thereof.

16. The method of claim 15 wherein the polybasic carboxylic acid is citric or tartaric acid.

17. The method of claim 11 wherein the molar ratio of aluminum ion to carboxylic acid is about 2:1 to about 10:1.

18. The method of claim 12 wherein the waters are treated with a flocculating agent comprising an aqueous solution having a concentration of about 2.0 to 10 mg/l of aluminum ion.

19. The method of claim 11 wherein the waters are treated with a flocculating agent comprising an aqueous solution of polymeric aluminum hydroxy-chloride and a polybasic organic carboxylic acid.

20. The method of claim 19 wherein the carboxylic acid is a citric or tartaric acid.

21. The method of claim 19 wherein the carboxylic acid is L-(+)-tartaric acid.

22. The method of claim 19 wherein the aqueous solution has a concentration of about 2.0 to 10 mg/l of aluminum ion and the molar ratio of aluminum ion to carboxylic acid is about 2:1 to about 10:1.

23. A method of flocculating planktonic algae in fresh waters down to a carbonate hardness of about 1°dH and an alkalinity of about 0.36 mVal/l without harming fish which comprises treating said waters with an effective amount of a flocculating agent according to claim 1.

24. A method a clarifying a body of water contaminated with an algal bloom comprising treating said body of water with an effective amount of a flocculating agent as described above.

INTERNATIONAL SEARCH REPORT

Internat. Application No.

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A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C02F1/52

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C02F

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,4 435 308 (THOMAS MARYVONNE ET AL) 6 March 1984	1-10
Y	see column 1, line 55 - column 2, line 35; examples 1,4,7-9	11-24

X	US,A,4 388 208 (GYTEL ULLA B) 14 June 1983	1-10
Y	see column 2, line 21 - column 2, line 53	11-24

X	US,A,4 536 384 (LINDAHL GERTRUD M) 20 August 1985	1-4
A	see claims 1-4; examples 1-3	5-24

A	US,A,5 296 213 (HAASE DIETER ET AL) 22 March 1994	1-24
	see column 1, line 32 - column 3, line 68	

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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4435308	06-03-84	FR-A- 2319583	25-02-77
		AU-B- 1638476	02-02-78
		BE-A- 844677	31-01-77
		CA-A- 1073774	18-03-80
		DE-A- 2634126	10-02-77
		GB-A- 1525139	20-09-78
		JP-C- 1031892	29-01-81
		JP-A- 52031989	10-03-77
		JP-B- 55023207	21-06-80
		LU-A- 75498	15-04-77
		NL-A- 7608434	02-02-77
		SE-A- 7608524	01-02-77
US-A-4388208	14-06-83	SE-B- 437016	04-02-85
		CA-A- 1172540	14-08-84
		EP-A,B 0062015	06-10-82
		JP-A- 57175729	28-10-82
		SE-A- 8101830	24-09-82
US-A-4536384	20-08-85	SE-B- 436276	26-11-84
		EP-A- 0125221	14-11-84
		SE-A- 8302386	29-10-84
US-A-5296213	22-03-94	AU-B- 667393	21-03-96
		AU-B- 4693393	15-03-94
		CA-A- 2140371	03-03-94
		WO-A- 9404462	03-03-94
		CN-A- 1082006	16-02-94
		DE-D- 69302479	05-06-96
		EP-A- 0655985	07-06-95
		FI-A- 950596	10-02-95
		JP-T- 7508490	21-09-95
		NO-A- 950514	10-02-95
		ZA-A- 9305445	28-03-94



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